CALCRETES

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1. Introduction

Calcretes or caliches are one of the types of non-marine carbonates that have received much attention from a variety of scientists including geomorphologists, pedologists and sedimentologists. This interest in calcretes results from their widespread occurrence in continental settings, and because they are important repositories of information about the reconstruction of past ecosystems and environments, and about the tectonic, climatic and sedimentary regimes in which they formed. Exhaustive reviews on calcretes have been provided by Esteban and Klappa (1983), Wright and Tucker (1991), Paquet and Ruellan (1997), Watson and Nash (1997), Alonso-Zarza (2003) and Wright (2007). The most important aspects of calcretes are clearly developed in these works. The present review aims to provide a concise summary of the general aspects of calcretes, such as classification, morphology, micromorphology and geochemistry, with a focus on their palaeoenvironmental significance for reconstructing geomorphic and stratigraphic controls.

A practical definition of a calcrete is that proposed by Watts (1980) after modifying that of Goudie (1973): 'pedogenic calcretes are terrestrial materials composed dominantly, but not exclusively, of $CaCO_3$, which occur in states ranging from nodular and powdery to highly indurated and result mainly from the displacive and/or replacive introduction of vadose carbonate into greater or lesser quantities of soil, rock or sediment within a soil profile'. This definition only refers to pedogenic calcretes. Wright and Tucker (1991) later proposed a wider use of the term 'calcrete' that is not restricted to pedogenic occurrences; in some semi-arid to arid regions, extensive precipitation occurs in the shallow phreatic zone and produces large bodies of authigenic carbonates with many of the characteristics of pedogenic calcretes and palustrine carbonates (see Alonso-Zarza and Wright, 2010). Where calcium carbonate is introduced into a non-carbonate host, its authigenic origin is clear, but calcretes can also develop in carbonate bedrocks and sediments, including those formed around lake margins, seasonal wetlands and groundwater-discharge zones, creating a spectrum of complex relationships (Tandon and Andrews, 2001; Alonso-Zarza, 2003).

2. Classification

The classification of calcretes is complex since various criteria may be used. Purely descriptive classifications consider mineralogy and morphology. A fundamental distinction must be made between calcretes that are formed in soil profiles within the vadose zone (pedogenic calcretes) and ones formed around the water-table capillary fringe or below due to laterally moving waters, in some cases at considerable depth (Carlisle, 1980, 1983). The former owe their origin to the addition or redistribution of calcium carbonate associated with eluvial/illuvial processes, whereas the latter are due to precipitation from groundwater (Arakel and McConchie, 1982), occasionally under the influence of phreatophytic plants (Semeniuk and Meagher, 1981), hence the term 'groundwater calcrete' (or phreatic, channel or valley calcrete). A less common type is referred to as 'gully bed cementation' and takes place where carbonate-rich run-off infiltrates channel sediments, leading to the plugging of the sediment layer by carbonate cement and the production of laminar layers (Mack et al., 2000). It is pedogenic calcrete that can show well-developed profiles and has received the most attention from researchers (Figure 1A and B). Groundwater calcretes may be difficult to distinguish from those formed under pedogenic conditions (Pimentel et al., 1996; Mack et al., 2000; Tandon and Andrews, 2001). In some cases, it may also be difficult to distinguish groundwater calcretes or dolocretes from carbonates formed due to the effects of non-exclusively meteoric diagenesis (Williams and Krause, 1998).

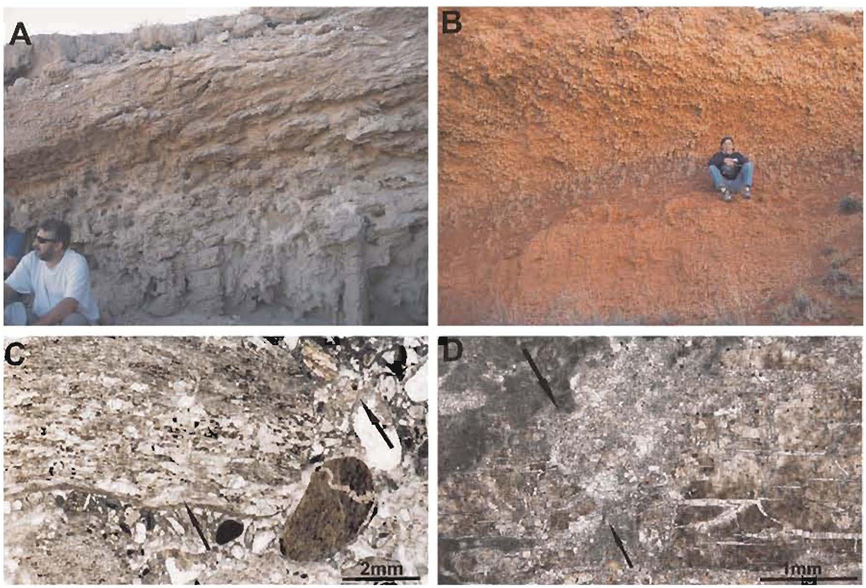

Figure 1 Calcrete macro- and micromorphology. (A) Thick pedogenic calcrete showing a lower nodular horizon and an upper laminar one forming a hardpan; they are separated by gravel clasts (Pleistocene of Gran Canaria, Spain). (B) Two pedogenic calcrete profiles (mostly nodular), separated by a bed of red clays that also contains calcrete nodules (the person is seated in this clay bed) (Palaeogene of the Teruel Basin, Spain). (C) Clasts of metamorphic rocks showing thin micritic coatings (arrowed) formed under the influence of microbial biofilms (Pleistocene of the Guadix Basin, Spain). (D) Coarse calcite crystals (arrows) replacing the feldspar that occupies most of the space (Palaeogene of the Sado Basin, Portugal).

Despite the wide use of the term 'calcrete' and its synonyms 'caliche' and 'cornstone' (Allen, 1960), and many more terms (Goudie, 1973), none are included in any soil classification, either as a soil name or as a horizon. Within a soil, the horizon of prominent carbonate accumulation has been named the K horizon (Gile et al., 1965); it has a diagnostic K-fabric. Pedogenic calcretes form within soil profiles where they constitute several discrete horizons of carbonate accumulation, forming a sub-profile within the main soil profile (Wright and Tucker, 1991). Aridisols, Vertisols, Mollisols and Alfisols (Soil Survey Staff, 1975) are the more typical soils containing calcretes (Wright and Tucker, 1991), developing in the B or C horizons as illuvial concentrations. In palaeosol classifications, calcrete-bearing palaeosols are considered Aridisols (Retallack, 1993), Calcisols (Mack et al., 1993) or palaeo-Aridisols (Nettleton et al., 2000).

With the dominant carbonate mineral and the amount of dolomite in mind, a simple classification was proposed by Netterberg (1980), who distinguished between calcretes, magnesian calcretes, dolomitic calcretes and dolocretes. The dominant mineralogy of calcretes is low-Mg calcite (Wright and Tucker, 1991), although complex reactions should be expected as a result of microbial and physicochemical processes (Watts, 1980). Dolomite is commonly recorded, being either primary or formed by replacement, but rarely constitutes the main mineral (Bustillo and Alonso-Zarza, 2007). In some groundwater dolocretes, dolomite may be the main mineral because it forms when the Mg/Ca ratio is high, which is more likely to happen in evolved groundwaters where Ca has been removed by precipitation of calcite. More complex carbonate mineralogies have been recorded from pedogenic carbonates associated with Mg-rich bedrock (e.g., Podwojewski, 1995) and volcanic rocks (Molina, 1988).

The morphology of calcretes and their different horizons has given rise to a large number of names (Netterberg, 1980; Goudie, 1983), which have been summarised by Wright and Tucker (1991). These include calcareous soil, calcified soil, powder calcrete, pedotubule calcrete, nodular calcrete, honeycomb, hardpan, laminar calcrete and boulder/cobble calcrete.

3. Calcrete Distribution

Soils in which significant amounts of calcium-carbonate accumulate are widespread at present. One estimate (Yaalon, 1988) suggests that such soils cover 13% of the Earth's land surface; in Australia, currently the driest continent, calcretes occupy 21% of the land surface (Chen et al., 2002), but this figure may include non-pedogenic forms. The distribution of groundwater calcretes on a global scale is not known. Calcium carbonate will accumulate in a soil where there is a moisture deficit, allowing any carbonate fixed in the soil during a dry season to survive leaching in seasons where rainfall exceeds evaporation. As organisms, especially plants and fungi, play a critical role in fixing carbonate, a critical aspect is the relationship of organic activity and the soil-moisture regime. There are certain relationships between the distribution of pedogenic calcretes and climatic regimes. For example, most such calcretes are found today in climatic regimes with a mean annual temperature of 16–20°C (Goudie, 1983), but they are also known from cold deserts, implying that rainfall is the critical factor. Most 'warm' calcretes form where the rainfall ranges between 100 and 500 mm (Goudie, 1983), but they can form in areas with higher rainfall, up to 1,000 mm (Mack and James, 1994). Other studies, such as that of Royer (1999), show that carbonate-bearing soils are mainly found where rainfall is <760 mm, but there are many exceptions to this pattern (Birkeland, 1999; Retallack, 2000). For example, Strong et al. (1992) document strongly biogenic calcrete features in soils from North Yorkshire in the UK where local highly permeable carbonate gravels have triggered soil-moisture deficits large enough to produce features typical of drier, warmer regions. Similar calcretes have been recorded from Pleistocene deposits from the UK from a phase of climatic amelioration within the Anglian (Elsterian, early Kansan) glacial stage (Candy, 2002). Thin calcretes are known today in Arctic areas (Lauriol and Clarke, 1999), in glacial tills from Antarctica (Foley et al., 2006), as well as from Pleistocene cold settings (Vogt and Corte, 1996).

Calcrete-bearing soils commonly support a sparse vegetation cover, including grasses, trees and shrubs. Goudie (1973) has compiled a wide list of species; many are xerophytic, but not all, and root development may vary from horizontal to oblique or vertical. Macroflora is the most obvious contributor to soil formation, but microflora and soil fauna are important, and commonly they start to prepare the soil for the colonisation of higher plants.

Calcrete profiles require long periods for their formation (see below), and climate changes may take place so that what is left as the final product in a well-developed profile might be the sum of many significant environmental changes (Wright, 2007). Indeed, once carbonate accumulates it may not remain as a record of the initial climatic phase, as shown by the Holocene calcrete-bearing soils of the Gangetic Plains (Srivastava and Parkash, 2002), where carbonate accumulations that had been formed around 6,500 BP under a dryer climate were removed over large areas during a more recent wetter phase.

The distribution of ancient pedogenic calcretes mirrors this modern day distribution in the sense that such examples are commonly found in ancient dry-land (especially 'red bed') successions. Ancient and recent calcretes from the Himalayas and India contain valuable palaeoclimatic information of several geological periods, including the Cretaceous (Ghosh, 1997), Palaeogene (Singh and Lee, 2007), Miocene (Ghosh et al., 2004) and Quaternary (Srivastava, 2001; Srivastava et al., 2007). The special significance of these calcrete-bearing palaeosols is that they provide palaeoclimatic data that may contribute to the understanding of the palaeomonsoonal regimes over time. Some ancient fluvial units such as the classic Old Red Sandstone in the southern UK contain hundreds of profiles representing tens of millions of years of non-marine deposition (Allen, 1986). They are also prominent features in many shallow-water carbonate successions, where they mark emersion surfaces (Wright, 1994).

4. Source of Calcium Carbonate and Mechanisms of Carbonate Precipitation

4.1. Provenance of calcium carbonate

Two main models have been proposed for the supply of carbonate to calcrete profiles (Goudie, 1983). In the '*per descensum*' model, the carbonate enters the profile in solution from the upper soil levels to a lower horizon; this is the common process in pedogenic calcretes. In contrast, carbonate obtained from groundwater defines the '*per ascensum*' model, which is dominant in phreatic calcretes. The Ca in pedogenic calcretes can be derived from many sources, including local rocks, rainwater, dust, the biota and sea spray in coastal areas (Goudie 1983; Cailleau et al., 2004). In most semi-arid and arid areas, the main source – excluding local rocks – must be dust and rainfall. Monger and Gallegos (2000) have, for example, evaluated the contributions from dust and rainfall in the Las Cruces region in New Mexico, noting that the main source of Ca is rainfall. However, the pathway of Ca into the soil may be complex, as some Ca may be fixed by the vegetation before later being released into the soil. Garvie (2004) has shown that a significant pathway could be cacti that concentrate Ca, which can be released later, when the plant decays (see below).

The sources of Ca can be assessed in calcretes using the $^{87}Sr/^{86}Sr$ ratios as proxies for the sources of Ca. Sr and Ca have similar chemical properties, and Sr therefore shows a strong affinity with Ca. This makes $^{87}Sr/^{86}Sr$ ratios a good tracer for the provenance of Ca (Dart et al., 2007). This ratio depends on the source of carbonate (e.g., old continental rock, volcanic rocks, marine carbonate, aeolian dust) (Quade et al., 1995). In one of the earliest applications in calcretes, Quade et al. (1995) were able to identify the sources of Sr for calcretes from coastal and inland areas in South Australia and Victoria; Sr isotopes revealed that, near the coast, the ocean was the principal source, but that volcanic sources were important locally, and that further inland the contribution of marine-derived Sr decreased, reflecting the addition of inland dust sources. In most cases, the contribution of the Ca from weathering of the host rock is minimum in comparison with the contribution of Ca from aeolian dust or atmospheric input (Chiquet et al., 1999; Capo and Chadwick, 1999; Naiman et al., 2000), even in the presence of adjacent marine carbonates (Hamidi et al., 2001). Only in some cases does the $^{87}Sr/^{86}Sr$ ratio of the carbonates yield values close to the silicate host rock, as in the calcrete of Tamil Nadu in South India (Durand et al., 2006); however, influx of Ca dust also contributed to the formation of that calcrete. If calcretes develop on silicate rocks, the chemical weathering of the minerals consumes CO_2, so pedogenic carbonates play an important role in CO_2 cycle as a possible sink for it (Lal and Kimble, 2000).

Groundwater calcretes and dolocretes are most likely to have complex sources, reflecting the geology in the drainage basin. Spötl and Wright (1992), measuring Sr ratios in Triassic dolocretes from the Paris Basin, France, concluded that the source was a complex basement terrain and not marine waters, as had previously been thought.

4.2. Mechanisms of accumulation

Pedogenic carbonate accumulation can generally be regarded as an eluvial/illuvial process (*per descensum* model of Goudie, 1983). Calcium carbonate in surface layers, mainly as dust, is taken into solution and infiltrates into the soil. Some may be transported in colloidal form (Baghernejad and Dalrymple, 1993). Calcium bicarbonate is also supplied directly via rainwater, and rarely from groundwater (Knuteson et al., 1989). However, it is clear that both biogenic and abiogenic processes are at work and result in soil carbonate with varied types of microfabrics (see below). The calcium carbonate added to the soil, by whatever mechanism, is emplaced in three ways. Firstly, if generated as distinct components in biofilms (Figure 1C), fungal mycelia, released from decayed cells, or as colloidal material, it constitutes a particulate component of the soil. Secondly, it can fill pore spaces in a passive manner as simple cement. Thirdly, it can be introduced as a displacive phase, commonly seen in non-carbonate hosts where the calcite, being unable to form adhesive bonds with non-carbonate grains (Chadwick and Nettleton, 1990), can displace the host grains (Figure 1D) to produce a range of macro- and micro-textures (reviewed by Wright and Tucker, 1991).

Abiogenic (inorganic) carbonate precipitation is driven by evaporation, degassing and evapotranspiration (Wright and Tucker, 1991). McFadden and Tinsley (1985) presented simulation models for inorganic carbonate precipitation, and by integrating climate data, soil properties and chemical thermodynamic relations it was possible to calculate the amount and depth of calcium carbonate depending on time. However, the models also have a biotic component because evapotranspiration controls the amount of water in the soil and respiration of soil organisms control the pCO_2 (Monger and Gallegos, 2000).

Apart from the influence on evapotranspiration, it appears that, in many calcretes, plants and other organisms drive most of the carbonate precipitation. This results from: (1) the production of metabolic products that favour carbonate precipitation in the vicinity of microbes (Callot et al.,1985; Phillips and Self, 1987); (2) the potential of some microbes to precipitate carbonate and so calcify, such as bacteria and cyanobacteria (Monger et al., 1991; Verrecchia et al., 1995; Loisy et al., 1999); (3) the ability of some plant roots to fix calcite in their cells, because this enhances the production of protons, helping the plants to obtain mineral nutrients (McConnaughey and Whelan, 1997; Kosir, 2004); and (4) termites (Monger and Gallegos, 2000), bees, wasps, earthworms and slugs that can help in the mobilisation and precipitation of carbonate within soils (Canti, 1998).

One other mechanism relates to the ability of plants and fungi to produce large amounts of calcium oxalates that can be altered by oxalotrophic bacteria and oxidised to calcium carbonate (Verrecchia et al., 2006). Whewellite (calcium oxalate monohydrate) can be fixed in cells and later converted via weddellite (calcium oxalate dehydrate) by microbial activity to calcite (Braissant et al., 2004).

5. Micromorphology of Calcretes

Literature on this subject is substantial, with many accessible reviews, such as those by Braithwaite (1983), Esteban and Klappa (1983), Wright and Tucker (1991), Wright (1994) and Alonso-Zarza (2003). The following is therefore only an overview of the main aspects of calcrete petrography. The micromorphology of calcretes reflects the processes, biogenic or non-biogenic (abiotic), that produce the precipitation of carbonate, although in most calcretes both types of processes have commonly operated to form both biogenic and non-biogenic features. In addition, in some cases, the ultimate origin of a specific feature may not be completely clear. Many of these features are documented from relatively young palaeosols or active soils and are not always preserved in ancient calcretes (Alonso-Zarza and Arenas, 2004). Wright (1990a) proposed two end-member microfabrics for calcretes. Biogenic features are dominant in beta microfabrics, whereas they are absent in alpha microfabrics, which are characterised by non-biogenic features.

5.1. Alpha microfabrics

Non-biogenic features are the result of supersaturated soil solutions, which may cause precipitation in pores, recrystallisation, replacement of carbonate and non-carbonate components of the soil (Braithwaite, 1989), and in some cases, multiple phases of calcite growth (Wright and Peeters, 1989) and dolomitisation. These features include crystalline carbonate groundmasses and the crystic plasmic fabrics of Brewer (1964), with crystal sizes from micrite to spar. The presence of patches with coarse crystals distributed irregularly amongst the micrite/microspar is common. Floating grains are mostly silicates, but can vary depending on the composition of the host; they are commonly etched and show evidence of grain expansion or fracturing. Different types of desiccation and shrinkage cracks, which may be filled with calcite cements, are also interpreted as non-biogenic, as are calcite rhombs (whose origin is not fully clear). Nodules are common in alpha calcretes, but their origin is difficult to establish. The sharpness of the nodules may be an indicator of their genesis. Nodules with diffuse margins may indicate that they formed abiogenically from meteoric waters (Khadkikar et al., 1998). However, it is not easy to distinguish between nodules formed biogenically from those formed abiogenically. In fact, many nodules have been interpreted as the result of carbonate precipitation around roots, which would imply that they are rhizoliths. Hence, care must be taken when interpreting the origin of nodules.

5.2. Beta microfabrics

Beta microfabrics are very diverse; features of these include the following nine types.

(1) Alveolar-septal structures are millimetre-sized arcuate micritic septa of variable length appearing within pores (Adams, 1980), bordering root traces (Klappa, 1980), or which appear intercalated between micritic laminae (Figure 2A) (Alonso-Zarza, 1999). The septa are formed either by equidimensional micritic crystals or by acicular needle-fibre calcite. Alveolar-septal structures are basically interpreted as the by-products of fungal activity formed in fungal mycelia commonly, but not wholly, associated with roots (Wright, 1986; Wright and Tucker, 1991).

(2) Coated grains (Figure 2B–D) are an important component which can be very variable in size (Hay and Wiggins, 1980). The nucleus of the grains can include relics of the host rock, micrite or even parts of alveolar-septal structures. The coatings are symmetrical or asymmetrical (Figure 2C). The formation of these grains requires the generation of the nuclei, either by desiccation or by root activity, and the formation of the coating, which is controlled by roots and associated micro-organisms, especially fungal filaments and cyanobacteria (Knox, 1977; Calvet and Juliá, 1983; Wright, 1990b; Alonso-Zarza et al., 1992a).

(3) Calcified filaments, which are often present in any type of calcrete (James, 1972; Kahle, 1977), consist of sub-millimetre sized straight or sinuous tubes, either single or with Y-shaped branching. The filaments are connected to each other, and may appear collapsed and coated by calcite crystals. They appear to be largely fungal in origin, but other

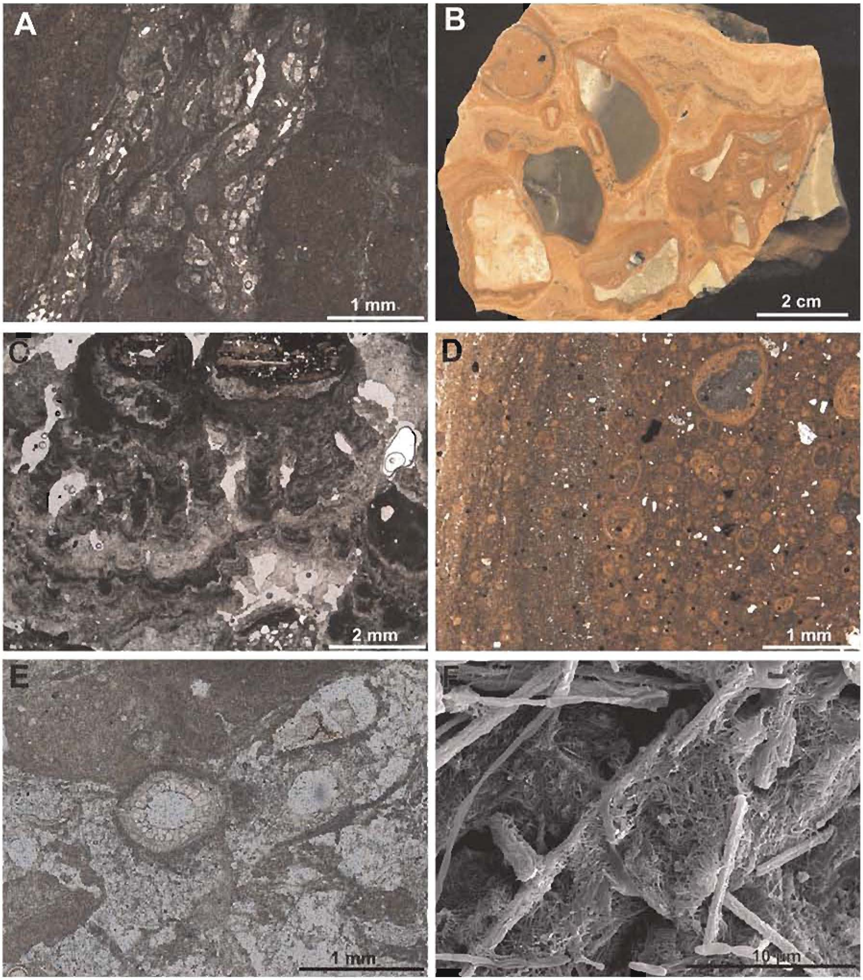

Figure 2 Biogenic features. (A) Alveolar-septal structure consisting of large interwoven micritic filaments; the porosity is filled by calcite spar (Miocene of the Teruel Basin). (B) Polished slab of a calcrete showing coarse gravel clasts and a topmost laminar horizon (Miocene of the Madrid Basin, Spain). (C) Asymmetrically coated (lower sides) gravel clasts (Teruel Basin). (D) Sand-sized micritic coated grains (Pleistocene of Canary Islands). (E) Root section showing calcified root cells (almost in the centre of the image); needle-fibre calcite crystals are seen in the lighter areas (recent calcrete in the neighbourhood of Brihuega, Spain). (F) Needle-fibre calcite crystals of different sizes; organic filaments (not collapsed) are also visible (same calcrete as E).

micro-organisms and root hairs may also form these filaments. Verrecchia et al. (1993) have demonstrated that, in some cases, biomineralised fungal filaments could have been composed of calcium oxalates that later were transformed to carbonate.

(4) Rhizoliths, calcified root cells and *Microcodium* are very common in calcretes (Figure 2E). They are discussed in detail in Klappa (1980) and Kosir (2004). The origin of *Microcodium* has been a matter of controversy. It is commonly interpreted as the product of calcification of root cells (Kosir, 2004), but some doubts have recently arisen on its rhizogenic origin (Singh et al., 2007; Kabanov et al., 2008).
(5) Needle-fibre calcite crystals are up to 10 μm wide and up to 200 μm in length, but can be very variable in size (Figure 2F). They vary from monocrystalline rods to polycrystalline chains, showing different morphologies (Verrecchia and Verrecchia, 1994). Their formation is due to either high levels of supersaturation or microbial activity, especially that of fungi or cyanobacteria (Callot et al., 1985; Phillips and Self, 1987) or specifically to the calcification of fungal sheaths (Bajnóczi and Kovács-Kis, 2006).
(6) Spherulites have been one of the most controversial features of laminar calcretes. They consist of low-Mg calcite fibro-radial spherulitic polycrystals, the diameter of which varies from 0.5 μm to more than 100 μm (Verrecchia et al., 1995). Contrary to some of the discussion on their origin (Verrecchia et al., 1995; Wright et al., 1996; Freytet et al., 1997), growth experiments and the fact that they occur at the very top of laminar calcretes support the idea that their formation is associated with cyanobacterial and bacterial mats that developed as thin films in ponds that later dried up, meaning they have to form at the sediment/atmosphere interface.
(7) Microborings are more or less cylindrical cavities of about 300 μm long and 1 μm in diameter. They have no preferred orientation and can be empty, coated by mucilage or lined by calcite crystals. They are similar in size and morphology to the porosity left by filaments or root hairs (Alonso-Zarza and Jones, 2007).
(8) Spherical to slightly polygonal bodies, 0.5–1 μm in diameter, with calcite walls of 0.1 μm thick have been attributed to spores (Jones, 1992; Alonso-Zarza and Jones, 2007) and bacteria (Alonso-Zarza and Arenas, 2004).
(9) Other biogenic features include those resulting from the activity of soil fauna, including such features as faecal pellets, and traces of bees, wasps, termites and ants. Some of these structures or ichofabrics are described in Genise et al. (2010).

Beta calcretes are only known really from the late Palaeozoic to the present, and it is surprising that more records are not available from the Devonian, during which there was significant plant cover. The occurrence of a specific biogenic feature is related to the presence of the organism that produced it, which was the case for the distribution of 'classic' *Microcodium* during the Cretaceous and Lower Tertiary (Klappa, 1978), whereas

Microcodium β is widespread in the geological record since the Carboniferous (Goldstein, 1988; Alonso-Zarza et al., 1998a). In addition, considerations of preservation potential, for example the effects of diagenesis on some of the delicate biogenic structures such as the spherulites or the needle-fibre calcite, cause these features to be more commonly recognised in recent (Quaternary) calcretes than in older rocks (Alonso-Zarza and Arenas, 2004).

6. Groundwater Calcretes

Groundwater calcretes are non-pedogenic carbonates whose formation is due to interstratal cementation, displacement and replacement of sediment bodies by carbonates within shallow aquifer systems (Netterberg, 1969; Mann and Horwitz, 1979). The mechanisms of carbonate precipitation are mostly evaporation, evapotranspiration, CO_2 degassing and the common ion effect (Wright and Tucker, 1991). Groundwater calcretes were initially referred to as 'valley calcretes' (Butt et al., 1977) to describe the massive carbonate bodies associated with drainage channels. However, this term may include both pedogenic and non-pedogenic types, so the terms 'groundwater calcretes'or 'phreatic calcretes' are generally preferred.

Extensive groundwater calcretes (widths of more than 50 km) are well documented (Chen et al., 2002). Their formation depends not only on the availability of water, but also on the permeability of the material that they replace. Their shape is controlled by the drainage topography (Mann and Horwitz, 1979). In general they vary in thickness from several centimetres (Tandon and Gibling, 1997) to several metres (Arakel, 1986). The identification of very thick groundwater calcretes (Pimentel et al., 1996) has not always been clear; in the Sado Basin, for example, originally considered thick groundwater calcrete beds were later interpreted as palustrine carbonates (Pimentel and Alonso-Zarza, 1999). However, recent work by Jutras et al. (2007) described massive phreatic calcretes (>10 m), from the Carboniferous of Canada, similar to those forming around salt lakes in Australia.

The morphology and characteristics of groundwater calcretes are varied, and sometimes difficult to differentiate from pedogenic calcretes (Figure 3A). The six main types of groundwater calcretes are described in the following paragraphs.

(1) The first type consists of thick massive beds of carbonate that have been deposited by the lateral flow of groundwater. The thicknesses are commonly >1.5 m (Mack et al., 2000), but some authors consider that the beds should be thicker than 3 m (Wright and Tucker, 1991) or even 10 m (Jutras et al., 2007). Regardless, this type is commonly referred to as groundwater calcrete; the microfabric is alpha-dominated, the lower

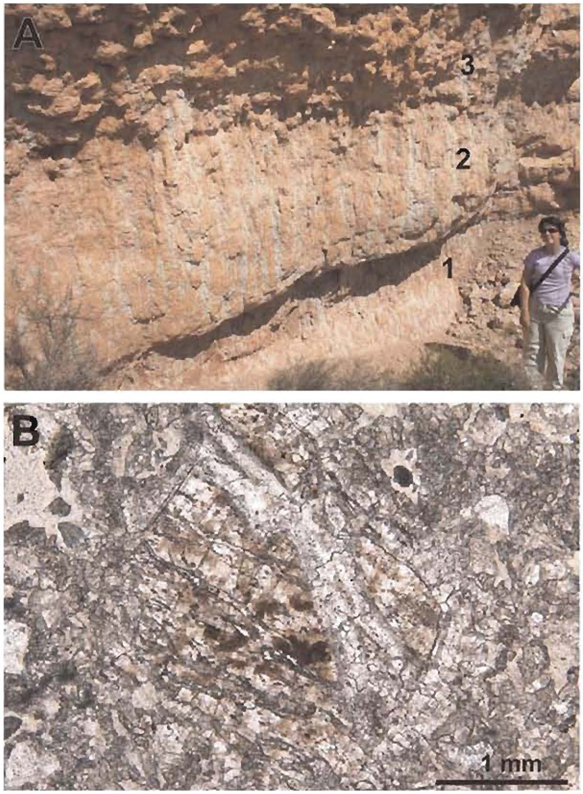

Figure 3 Groundwater calcretes. (A) Groundwater calcrete developed on previous pedogenic ones (1 and 2). Lighter vertical traces are due to roots. The deposition of a thin fluvial gravel bed (3) favoured the rise in groundwater and subsequent cementation of 1 and 2 (Miocene of the Madrid Basin). (B) Quartz grain etched and partially displaced/replaced by calcite (Sado Basin).

boundary is sharp and there is intense cementation and replacement of sediments by carbonate (Jutras et al., 2007), either calcite or dolomite (Spötl and Wright, 1992). This type of calcrete is classically described from around modern salt lakes in Central Australia (Arakel and McConchie, 1982; Arakel, 1986; Jacobson et al., 1988). In some cases, upward displacive growth of carbonate creates isolated or coalescent gentle mounds (Mann and Horwitz, 1979).

(2) The second type consists of soft carbonate nodules with diffuse boundaries that occur in layers which conform to the stratification of the sediment body, or which follow stratal planes of channels and mimic the convex geometry of the channel-fill deposits (Khadkikar et al., 1998).

(3) Cemented layers forming lenses up to 20 cm thick and 3 m long are the third type. They contain locally vertically elongated nodules (Tandon and Gibling, 1997). In some cases, they have an upper fringe of nodules and tubules precipitated at the water table and in the capillary fringe (Mack et al., 2000).
(4) Cemented proximal and medial alluvial fan facies as well as fluvial channels have been considered as a fourth type of groundwater calcretes (Tandon and Narayan, 1981; Nash and Smith, 1998). Their thickness and extent depend on the dimensions of the sedimentary body which undergoes cementation.
(5) The fifth type consists of thin calcified root mats; these have been included as groundwater carbonates because they may have been developed by phreatophytes in relation to very surficial, perched groundwater tables (Semeniuk and Meagher, 1981). In the Upper Cretaceous of India, for example, a shallow groundwater table favoured the formation of both root mats and gleyed horizons (Ghosh, 1997).
(6) Thin sheets (10–50 cm) in the subsurface of fluvio-aeolian sands (Purvis and Wright, 1989) form the sixth type. These sheets consist of aggregates of calcium carbonate developed just above the water table, so they may transect stratigraphic boundaries and unconformities (Semeniuk and Meagher, 1981).

Several attempts have been made to identify criteria to differentiate between groundwater and pedogenic calcretes (Wright, 1995; Pimentel et al., 1996). Groundwater calcretes commonly show sharp basal and top contacts. They are mostly massive bodies lacking any internal horizons. They commonly lack vertical root traces and peds (Mack et al., 2000), and are not overlain by horizons of illuviated clays (Mack and James, 1992). They also lack lacustrine biota or any indication of carbonate precipitation within a free water body. Groundwater calcretes are more common in more permeable coarse channel sediments (Nash and McLaren, 2003; Wright, 2007).

The micromorphology of groundwater calcretes is characterised by the absence of biogenic features. They are therefore encased in the so-called 'alpha' microfabrics (Wright and Tucker, 1991). They consist frequently of crystalline mosaics, with crystals varying in size from microns to millimetres, etched and floating grains (Figure 3B), nodules and a variety of desiccation features. The chemistry of phreatic water controls the mineralogy of the groundwater precipitates. In the proximity of the catchment areas, groundwater is commonly of low salinity and calcite is the main precipitate, but groundwater movement from the catchment area down to the playa-lake marginal discharge areas favours progressive concentration (Arakel, 1986). Changes in groundwater chemistry explain the formation of groundwater dolocretes and gypcretes towards the distal part of closed basins (Arakel, 1986; Armenteros et al., 1995; Schmid et al., 2006; Khalaf, 2007). Groundwater dolocretes show a wide range of crystal sizes and include spheroidal (Spötl and Wright, 1992) and zoned dolomite crystals, as well as dolomite with cloudy nuclei (Pimentel et al., 1996). Groundwater-dolocrete formation may also be favoured by the mixing of groundwaters and lake brines (Colson and Cojan, 1996), or with sea water (Williams and Krause, 1998). Barite is uncommon but found where groundwaters are more saline (Khalaf, 2007).

Groundwater calcretes generally occur in arid to semi-arid climates. Climate controls their formation for three reasons (Mann and Horwitz, 1979): (1) conditions of continual moisture favour carbonate dissolution, not concentration; (2) intermittent heavy rains tend to form better groundwater systems (due to more effective infiltration) than the equivalent rainfall spread over a longer timespan; and (3) high evaporation and evapotranspiration rates are essential for chemical precipitation of carbonate. In Western Australia, the active zone of groundwater formation occurs where the water table lies at depths of 2–5 m. In such arid environments, evaporation and evapotranspiration from the water table are insignificant below 5 m.

Rates of groundwater calcrete formation are difficult to establish, because the relationships with the under- and overlying sediments are not necessarily ordered stratigraphically, that is, groundwater calcrete is commonly younger than the overlying sediments. Whatever the case, as groundwater calcretes are supplied by calcium carbonate from the phreatic waters, and not limited by atmospheric input or weathering, it is likely that the rate of formation exceeds that of pedogenic forms (Wright, 2007). For example, studies on the Kalahari calcretes have effectively shown that 4-m-thick groundwater calcretes may form in less than 3,000 years (Nash and McLaren, 2003).

7. Pedogenic Profile Development

7.1. The idealised or classic profile

Gile et al. (1966) proposed that the morphology of calcic soils can be seen as a sequence of morphological stages that reflect the different degrees of development (relative time of development) of the soil. Within Stages I–III, the gravel content is important and is different in fine and coarse clastic deposits (Figure 4A). In gravel-rich calcic soils, Stage I is characterised by a thin, discontinuous coating on pebbles. In Stage II, the coatings are continuous and vary in thickness. Massive accumulations between clasts and fully cemented gravels are included in Stage III. In gravel-poor soils, Stage I shows few filaments or faint coatings on ped surfaces. Soft nodules, 5–40 mm in diameter, are indicative of Stage II, whereas coalescent nodules

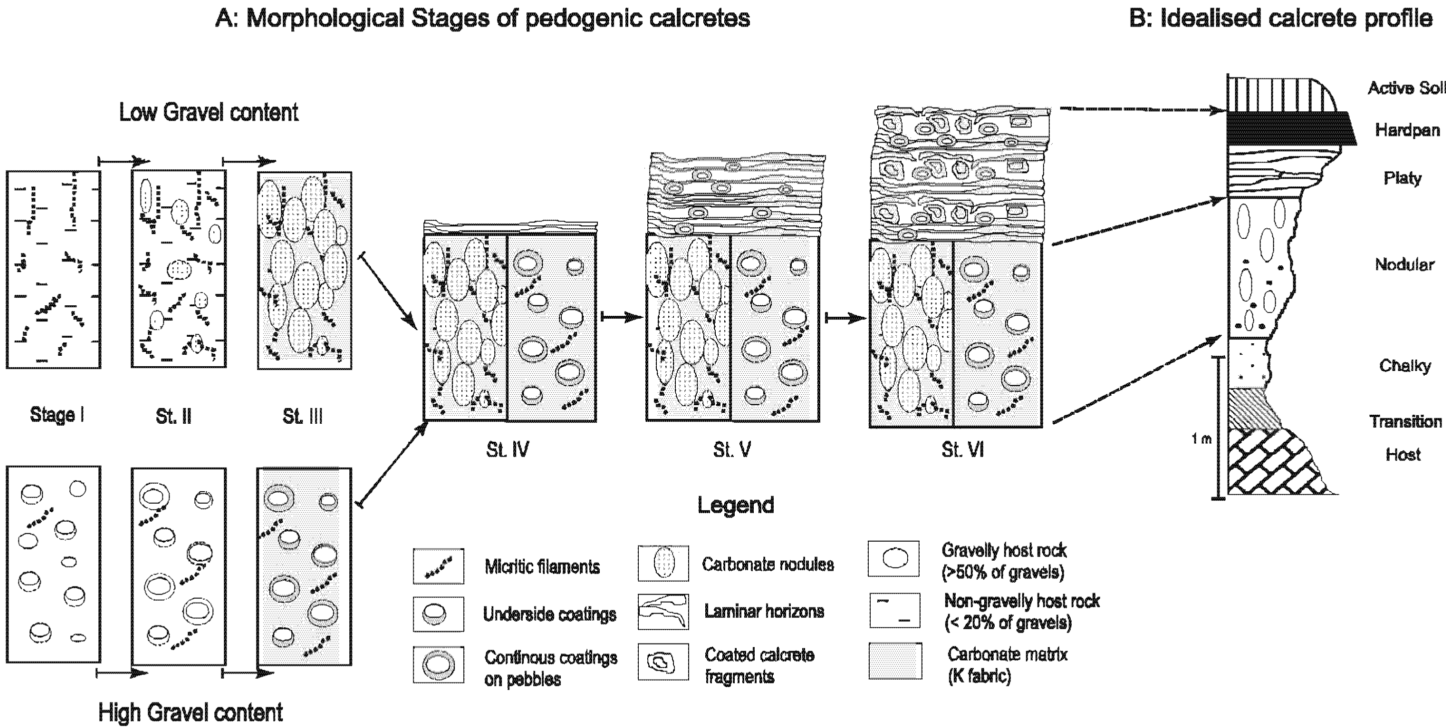

Figure 4 Stages of development of pedogenic calcretes (modified from Alonso-Zarza, 2003). (A) Based on Machette (1985). (B) Schematic idealised pedogenic profile (Esteban and Klappa, 1983), showing the relationship between the different horizons and the more advanced stages of development.

characterise Stage III. Machette (1985) established six stages, the first three similar to those previously established by Gile et al. (1966). Stage IV is characterised by carbonate-rich laminae less than 1 cm thick. Thicker laminae and pisoliths are indicators of Stage V, while Stage VI is characterised by multiple phases of brecciation, pisolith formation and recementation.

Based on numerous observations, Esteban and Klappa (1983) described an idealised calcrete profile (Figure 4B), in which the stages of formation of the different horizons are similar to those of the Gile et al. (1966) and Machette (1985) models. The profile consists of the following horizons (from base to top and including the host).

(1) *Host material.* This may be of any composition, texture and degree of compaction. Permeability and calcium-carbonate content may affect the degree of calcrete development (Wright, 1990c). The host material lacks any calcrete features and so is distinguished from the overlying calcrete horizons.
(2) *The transitional horizon.* This is the zone of *in situ* weathering of the host through mechanical, physicochemical and biological processes to form a regolith of weathered detritus. Relic primary structures of the host are commonly preserved. Its lower boundary is difficult to define and lies between the host material and the well-defined uppermost calcrete horizons. It indicates incipient soil development through changes produced by the action of organisms and by the movement of water through the host rock.
(3) *Chalky horizon.* This is a soft horizon consisting of a micrite and/or microspar matrix that contains etched detrital grains and peloids. It tends to be homogeneous, texturally and structurally, although some nodules are spatially related to roots. It is commonly located between the transitional and the nodular horizons, but it may occupy any other position within the profile or be absent. Precipitation of carbonate without significant induration leads to the formation of this horizon.
(4) *Nodular horizon.* This horizon is formed by powdery to indurated nodules of calcium carbonate embedded in a less carbonate-rich matrix. The nodules vary in morphology between vertical, horizontal, irregular or even branching. In cases where the nodules are vertically elongated (Figure 5A), the horizon is sometimes called the 'prismatic horizon'. Nodular horizons tend to show diffuse lower and upper boundaries (Figure 1B). Microscopically, the nodules are composed of micrite rich in etched grains, relics from the host material. Coated grains in which the nucleus is an etched grain are also common. Carbonate precipitation takes place in discontinuous areas in close association with roots and related micro-organisms. The biological components of the soil become calcified, forming rhizoliths, calcified filaments and

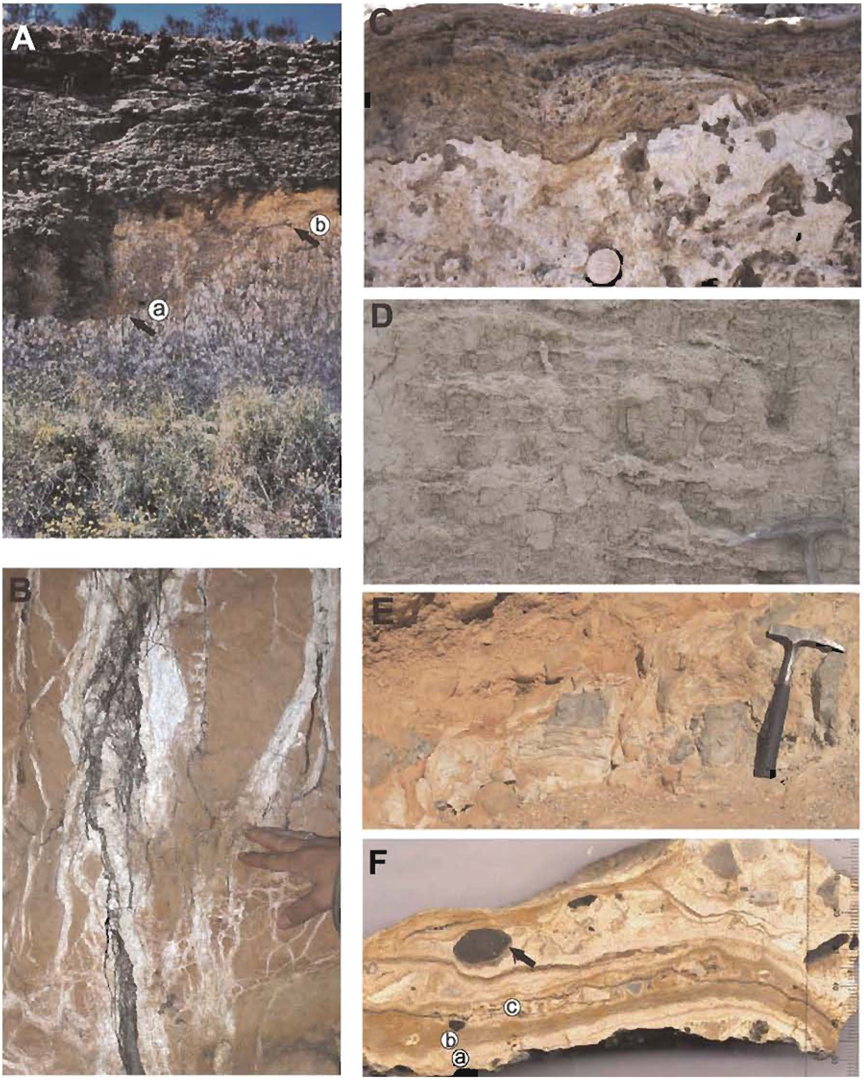

Figure 5 Laminar calcretes. (A) Thick 'multi-episodic' calcrete profile. The nodular horizon is partially eroded and the trough is filled by coarse sand (a). The laminar horizon is situated at the top. Although the nodular and laminar horizons are in lateral contact (b), important erosion is recorded in this calcrete (Pleistocene, Murcia, Spain). (B) Vertical calcrete development by penetration of tree roots (recent, Brihuega). (C) Laminar calcrete at the top of a limestone bed. The contact is very irregular (Quaternary, Florida). (D) Incipient laminar calcrete interbedded with clays (Miocene, Madrid Basin). (E) Calcrete developed at the Jurassic/Palaeogene unconformity; coarse coated clasts are visible (Teruel Basin). (F) 'Multi-episodic' laminar calcrete. Laminated micrite (a and b) alternate with laminae containing gravel and sand-sized clasts (c). Some of the clasts show coatings (arrowed) at their lower sides (Teruel Basin).

nodules. Vertical water movements and vertical root systems favour the formation of vertically oriented carbonate nodules. Initially they are much dispersed, but with time they coalesce to form the nodular horizon. These processes lead to the formation of the morphological Stages I–III of Machette (1985).

(5) *Platy horizon*. This commonly occurs overlying the nodular horizon (Figure 5A). When a hardpan is present at the top of the profile, the platy horizon underlies it. However, if a hardpan is lacking, the platy horizon is the topmost horizon of the calcrete profile. This horizon has also been called the 'laminar horizon'. Some calcretes composed almost exclusively of the laminar horizon are named 'laminar calcretes'. These are discussed in more detail below. The platy or laminar horizon has a wavy to thinly bedded habit, planar fracture porosity, and an abundance of alveolar-septal structures, rhizoliths and needle-fibre calcite. Internally, the different laminae show varied microfabrics that include micritic layers, micritic layers with tubiform pores, laminae very rich in alveolar-septal structures and laminae including micrite coated grains.

Once the nodules coalesce to form a dense horizon, root systems cannot easily penetrate the nodular horizon. In addition, water is mainly confined to the uppermost part of the profile in the still-unconsolidated zone above the nodular horizon. The morphology of the root systems therefore changes. Roots trying to maximise the amount of water they absorb tend to extend laterally, promoting the development of sub-horizontal networks. The laminar horizon starts to form in the still-unconsolidated zone. This stage includes Stages IV and V of Machette (1985).

(6) *Hardpan*. In very well developed profiles, this is commonly the topmost horizon. It is well indurated and the porosity is very low. Macroscopically it may be structureless, massive, laminated (Figure 1A) or nodular. This horizon is commonly formed by micrite containing corroded grains that are rarely coated. Laminated micritic layers may also be present. Thick hardpans are commonly fractured and brecciated, allowing the identification of the *brecciated horizon* (Stages V and VI of Machette, 1985). Differentiation between the platy horizon and the hardpan may be difficult, but hardpans have a more massive appearance in the field.

(7) *Pisolithic horizons*. These consist of sand- or gravel-sized clasts coated by laminated micrite and are very common in calcretes developed on coarse-grained host rocks (Figure 2B). In many cases, the horizons follow the geometry of the coarse deposit on which they developed (Alonso-Zarza et al., 1998b). The micrite laminae may coat all the clasts or only their undersides. The laminae are composed of dense micrite, micrite with alveolar-septal structures and/or microspar. The coated clasts are embedded in a dense matrix of irregular masses of microspar including some detrital grains and micrite with alveolar-septal

structures. Pisolithic horizons are common at the top of the calcrete profile when intense brecciation favours the formation of calcrete-sourced clasts, but also occur interbedded within the profile.

7.2. The rhizogenic model: laminar calcretes

Studies carried on in various calcretes from southern Europe (Wright et al., 1988, 1995) have shown that isolated (in millimetres) to thick (>2 m) laminar calcrete beds can form through the calcification of root mats. The root mats show fenestral textures representing fine root tubules with or without alveolar-septal structures, but in other cases, they are formed entirely of *Microcodium* remains.

Laminar calcretes may occur in different situations (Figure 5A–E): (1) at the top of thick calcrete profiles, but below the top soil (Figure 5A), (2) cutting any rock or sediments, being oblique to the stratification or even with a mainly vertical development (Figure 5B), (3) at the top of any bedrock (Figure 5C) or (4) interbedded within sedimentary deposits (Figure 5D). The formation of these laminar calcretes has been widely discussed (Verrecchia et al., 1995; Wright et al., 1996; Freytet et al., 1997; Alonso-Zarza, 1999), and there is a substantial consensus that they should be interpreted as rootcretes (Jones, 1992) or rhizogenic calcretes (Wright et al., 1995), since it is commonly accepted that the main agents responsible for their formation are horizontal (Mack and James, 1992; Wright et al., 1988) and vertical (Alonso-Zarza and Jones, 2007) root systems. However, when the calcretes occur at the top of the soils or bedrock, other organisms can operate. Cyanobacteria (Vogt, 1984; Verrecchia et al., 1995), bacteria, fungi (Verrecchia and Verrecchia, 1994) and lichens (Klappa, 1979) may account for the formation of laminar carbonate horizons.

Laminar calcretes can be misinterpreted as stromatolites (Wright, 1989). The main features of calcretes that allow their differentiation from stromatolites are: (1) the laminae are very irregular and show micro-unconformities attributable to phases of dissolution (Wright, 1989); (2) the laminae include etched grains, ooids and clays; (3) rhizoliths, alveolar-septal structures and spherulites are very common in laminar calcrete horizons (in some cases they may form the whole horizon) (Wright et al., 1988); and (4) alternations between micrite laminae and others rich in detrital sediments, ooids or coated micritic grains are common (Fedoroff et al., 1994; Sanz and Wright, 1994). Calcified filaments are common in both laminar calcretes and stromatolites, but in the latter they are commonly oriented perpendicular to the lamination, whereas in calcretes they show no preferred orientation.

When laminar calcretes occur at the top of a calcrete/soil profile or at the top of any type of bed rock (Figure 5E), their formation may be controlled by the presence of shallow-water tables and thin pond-water films on top of the soil surface. Very commonly, these calcretes contain spherulites and features related to the calcification of algae and/or cyanobacteria, which are phototrophic communities (Verrecchia et al., 1995). Both biochemical and physicochemical processes can contribute to the lithification of the laminae, for example through the precipitation of micrite by increased carbonate concentration of the ponded or capillary zone water, and also to the formation of non-pedogenic structures, such as coarse spar calcite cements. As laminar calcretes form at the soil/atmosphere interface, their presence indicates phases of direct subaerial exposure (Blumel, 1982) and so may reveal a phase of exhumation of the soil or bed rock.

7.3. Alteration model

This model relates to calcrete development on a calcareous host and does not involve the net addition of carbonate to the soil profile, but involves largely the redistribution of existing carbonate, although some new material is likely to have been added. As discussed by Rabenhorst et al. (1991), the calcrete development is via an alteration front. No clearly defined stages occur comparable to those seen in Aridisols as discussed above. In studies of calcretes developed on weakly consolidated Quaternary limestones in carbonate terrains such as the Bahamas and Yucatan, a key feature of profile development is the formation of calcrete stringers and mottled textures (Wright, 1994). In the case of the latter, the lack of displacive growth of carbonate leads to mottling effects in the porous host, rather than to nodule development. Stringers are calcified root zones and can be very extensive, being traceable in anastomosing sets for tens of metres or more within the profile in excavations of cliff sections.

7.4. Calcrete dynamics: sedimentation/erosion/calcretisation relationships

Classically calcretes have been interpreted as a result of continuous and aggrading pedogenesis in which the ratio between sedimentation rate and calcrete development results in the different stages of calcrete development (Leeder, 1975; Wright and Marriott, 1996). Even if the rainfall and the atmospheric input of carbonate could remain constant during long periods of time, the position of the land surface relative to the zone of carbonate accumulation in the soils is unlikely to have remained unchanged (Wright, 2007). Studies of Quaternary (Alonso-Zarza et al., 1998b) and even Palaeozoic (Marriott and Wright, 1993) calcretes have revealed the interplay of pedogenesis, episodic sedimentation and erosion. The interplay of these processes can be imprinted at a profile-horizon scale (decimetres to metres), and even at very small scale, such as the individual laminae (millimetres to centimetres) of the laminar calcretes (Figures 5F and 6) (Alonso-Zarza and Silva, 2002).

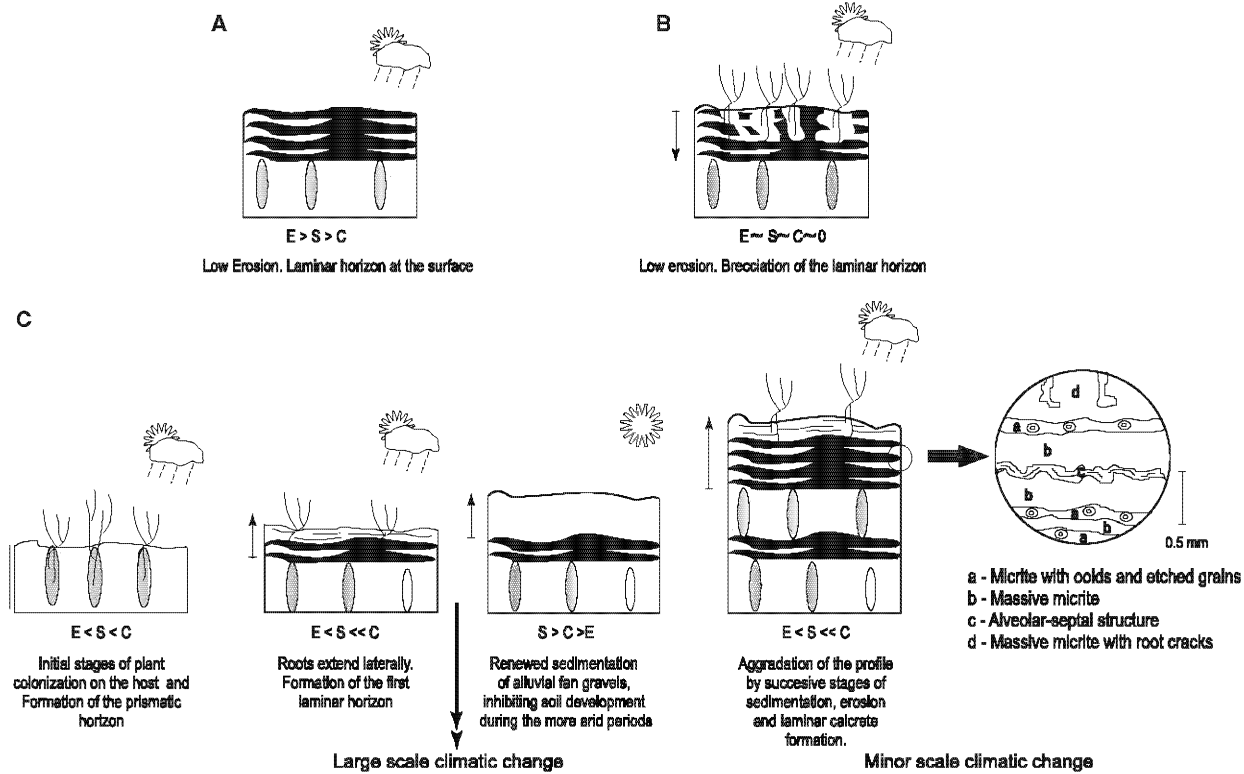

Figure 6 Final stages of the development of calcrete profiles depending on the overall rates of E (erosion), S (sedimentation) and C (calcrete formation). (A) Erosion is low, but higher than sedimentation, and calcrete formation is very slow. The development will finish with the exposure of the laminar horizon. (B) If erosion, sedimentation and calcrete formation are all close to zero, the result is the brecciation of the laminar horizon. (C) The development of thick calcrete profiles includes complex processes, with phases of erosion and sedimentation during the calcrete formation, so thick laminar calcrete profiles will form. Small-scale climatic changes cause the formation of different microstructures in the same laminar horizon, whereas larger scale changes will induce changes in the main horizon (from nodular to laminar). Different E, S and C ratios are shown to indicate how they interplay to form thick calcrete profiles. Based on Alonso-Zarza et al. (1998b) and Alonso-Zarza and Silva (2002).

At the profile-horizon scale, calcretes may be relatively complex, as similar horizons may occur at different positions within the calcrete profile, indicating composite profiles. In contrast, significant horizons may be lacking due to truncation by erosion during profile development (Alonso-Zarza et al., 1998b). Erosion causes reworking and the lowering of the carbonate profile by leaching and translocation to lower levels (Elbersen, 1982). In some cases, small-scale channel incision has truncated calcrete horizons, and the channel deposits have later been capped by a laminar calcrete that extends from the truncated to the non-truncated parts of the profile (Figure 5A). This indicates the complexity of calcrete profiles at the local scale of some profiles, as such erosive events that cause incompleteness may be not recognised.

The formation of thick calcrete profiles is often the result of several phases of erosion, soil formation and sedimentation (Alonso-Zarza and Silva, 2002) which, in many cases, are repeated over time. This is especially noticeable in the development of calcretes with a thick laminar calcrete at top (Stages V and VI). The degree of development, as well as the characteristics and thickness, depend on the time the root systems can be supported in the upper soil horizon. Alonso-Zarza et al. (1998b) considered the following three different situations (Figure 6).

(1) Cases where the erosion rate is low but exceeds the sedimentation rate. The upper part of the calcrete profile (B horizon) is removed and the laminar horizon is exposed directly to the atmosphere (Figure 6A). Lichens (Klappa, 1979), spherulites may grow in these superficial conditions, even in the presence of thin water bodies. Karstic microforms may also be present.
(2) Erosion and sedimentation at the top of the profile are reduced. Accumulation of calcium carbonate is continuously increasing, replacing even the uppermost soil. Once the top of the soil is totally replaced, there is no space any more for new carbonate accumulation, so calcrete development is inhibited. Pedogenic and later diagenetic processes lead to the lithification of the soil profile and to the formation of the hardpan. Later weathering of the profile causes the brecciation of the uppermost part (Figure 6B). This is Stage VI of Machette (1985).
(3) Deposition is low and episodic, but exceeds the erosion rate. This contributes new surface sediments for soil organisms and the subsequent development or maintenance of root systems. This favours the formation of very thick laminar horizons (Figure 6C); these do not represent individual events, but rather the addition of multiple phases of sedimentation and soil-formation processes, giving place to the formation of thick, cumulate profiles, such as those described from the western USA (Machette, 1985) or the Pleistocene of the Canary Islands (Alonso-Zarza and Silva, 2002).

At a lower scale (millimetres to centimetres), these laminar calcretes are formed by centimetre-scale alternations in which the different laminae may consist of micritic layers, micritic layers with fine tubiform pores, ooids, detrital grains and clays, and/or of micrite with an alveolar-septal structure (Figure 6C). These alternations reflect the small-scale periods of sedimentation, erosion and soil formation (Fedoroff et al., 1994) in the upper part of a relatively stable surface, and may indicate climate-related vegetation changes (Alonso-Zarza and Silva, 2002). The occurrence of these laminae interbedded with detrital sediments characterises environments in which sedimentation was slow and episodic. Therefore, after detrital sediment input, the surfaces became stable and root mats developed. Renewed sedimentation accounted for the development of new laminae on the new surfaces. The formation of these calcretes is essentially through vertical aggradation of successive laminae of ooids, sediment and massive micrite towards the top of the profiles (Figure 6C).

Less is known about the dynamic behaviour of calcrete profiles on carbonate substrates. Both Davies (1991) and Sattler et al. (2005) recorded a marked lateral variability in the types of calcrete development at exposure surfaces in Carboniferous and Cretaceous successions, respectively. These differences likely reflect local micro-topographic differences and preservational effects. Budd et al. (2002) noted that, in their studies of the development of macroscopic features at a range of carbonate exposure surfaces of different durations, the types of features developed were not directly related to the duration of exposure. These studies indicated that a simple model of calcrete development as a linear progression, rather like the illuvial models of Gile et al. (1966) and Machette (1985), may not apply to calcretes developed in carbonate-platform settings.

8. Calcretes in Quaternary Landscape Systems

Many of the 'classic' studies on the use of soils – and specially calcretes – for local and regional correlations are based on Quaternary case studies. The work of Machette (1985), in calcic soils of the southwestern USA, demonstrated that the total-profile index of secondary carbonate can be used to correlate and differentiate Quaternary sediments, to estimate the age of pedogenic calcretes, and even to estimate the recurrence intervals and the frequency of fault movements across fault zones.

Absolute dating of Quaternary calcretes allows more precision in the establishment of the time needed to form the different morphological stages. Radiocarbon dating of Quaternary calcretes has been carried out by several authors (Rowe and Maher, 2000; Deutz et al., 2002, amongst many others), pointing out the problems of mixing and later alteration by diagenesis, but providing good results. In addition, the development of the

U–Th series method since the last decade allows the determination of the age of calcretes with certain accuracy. The age is calculated from $^{230}Th/^{234}U$ and $^{234}U/^{238}U$ ratios of the sample (Ivanovich and Harmon, 1992). Uranium is very soluble in oxidised groundwaters, and co-precipitate with calcium during calcrete formation, whereas ^{230}Th, is immobile in near-surface environments and does not co-precipitate in the calcrete. The subsequent increase of ^{230}Th provides a tool to measure the time since carbonate was precipitated because it is produced later on. The upper limit of the technique is 350 ka (Rowe and Maher, 2000). This method has been applied to date calcretes in alluvial terraces of the Sorbas Basin in Spain (Kelly et al., 2000; Candy et al., 2004). In addition to U–Th, the U–Pb system can also be used to date much older calcretes (Wang et al., 1998; Rasbury et al., 2006), with different grades of uncertainty from more than 20 Ma to less than 3 Ma. The maximum age of calcretes that can thus be dated reliably may reach the Carboniferous (Rasbury et al., 2000).

In the Cinca and Gállego rivers, southern Pyrenees, calcretes that developed on stabilised surfaces on terraces, show a clear tendency of enrichment of carbonate from the lower to the upper terraces. The chronological data obtained by palaeomagnetism and luminiscense indicate that Stage I forms in 10 ka, while Stages IV and V need 600–800 ka (Sancho et al., 2004).

The calcrete developed at the top of the infill of the Guadix Basin has provided numerous data for discussion. Its age (42.6 ± 5.6 ka) is considered to be the age of the cessation of the active sedimentation within the basin. Since then, the incision of the Arroyo Gor began, and the calcrete age gave an estimation of the incision rate which was high (4 mm year^{-1}) (Azañón et al., 2006). Detailed isotopic analyses in this laminar calcrete also suggest different processes of formation of the laminae, which are the result of differences in climatic conditions. The massive micritic laminae show the heaviest carbon- and oxygen-isotope values and represent the most arid conditions, whereas laminae dominated by alveolar-septal structures are lighter in carbon, which is interpreted as an indication of a denser vegetation cover under a less arid climate.

Similar climatic alternations seem to be reflected in many Quaternary calcretes, as in those described from the Canary Island (Alonso-Zarza and Silva, 2002). However, more studies are needed to better constrain the climatic conditions and the time represented by each lamina. In doing so, Quaternary calcretes will potentially provide good data sources for the interpretation of the effects of climatic changes that can be applied to older calcretes. For example, the presence of poorly developed calcretes containing megarhizoliths in the aeolianites of Gran Canary in the Canary Islands has been considered as a proof that less arid conditions prevailed during certain Quaternary periods, allowing the development of a sparse vegetation cover (Alonso-Zarza et al., 2008). Pedogenic Quaternary calcretes also appear as bodies of restricted lateral continuity on colluvial deposits. In this case, calcretisation is a response of the periods of lesser tectonic activity and greater stability of the slope (Jiménez-Espinosa and Jiménez-Millán, 2003).

Groundwater calcretes are common in mudflat environments of playa lakes that act as outlets for discharge of regional groundwater (Arakel, 1991) in the vicinity of evaporitic basins (Jutras et al., 2007), as well as in different types of alluvial fans (Mack et al., 2000). Groundwater calcretes influence the evolution of the fan and overall drainage network (Nash and Smith, 2003). This is because both the decrease in water/sediment supply and the calcrete lithification may isolate the alluvial fans from the main drainage network (Stokes et al., 2007), favouring stable surfaces and pedogenic development (Nash and Smith, 1998; Wright, 2007).

Mixing between groundwater and pedogenic calcretes is common in alluvial fan and fluvial deposits. Groundwater cementation commonly occurs from the boundary with the finer deposits towards the top of the gravel channels, whereas pedogenic calcretes occur at top of the fluvial channels and finer deposits to the base of the sedimentary bodies. Pedogenesis occurs after the sedimentation and preceding the following sedimentary bed. On the contrary, groundwater cementation may proceed in different periods. In some cases, the increase of tectonic activity may introduce increased amounts of groundwater through the more permeable beds, favouring groundwater calcrete formation (Stokes et al., 2007). Mixed pedogenic and groundwater calcretes are also common in the deposits of interfluve channels in Late Quaternary interfluves from the Ganga Plains (Sinha et al., 2006). Their distribution in the alluvial architecture is a response to aggradation and degradation of the plains caused by monsoon-driven rhythms. The common imprint of pedogenic effects on groundwater features and vice versa offers new data for a better understanding of the overall alluvial system; groundwater calcretes must therefore be included within the pedo-stratigraphic models for alluvial fans (Stokes et al., 2007).

9. Calcretes in a Stratigraphic Framework

The spatial variability of pedogenic calcrete development within a sedimentary basin will ultimately reflect variations in the residence time in the soil of the zone of carbonate accumulation, as well as the particle size of the host sediment (Wright, 2007). These factors are controlled by the sedimentation, subsidence and calcretisation rates, which are all strongly related to tectonism and climate. Erosive processes must also be considered. When erosion is insignificant, the variation in palaeosol types is a response to the type and rate of sedimentation versus the rate of pedogenesis

(Marriott and Wright, 1993). If sedimentation is rapid and unsteady, weakly developed and vertically stacked profiles separated by minimally weathered sediment (compound palaeosols) form. Vertically successive profiles may partially overlap (composite palaeosols) if the rate of pedogenesis exceeds the rate of sedimentation. If sedimentation is steady, thick cumulative soils can form (Marriott and Wright, 1993; Kraus, 1999); thick laminar calcretes are a good example of this situation (Alonso-Zarza et al., 1998b). The presence or absence of a particular genetic stage of calcrete may be used as a rough estimate of ancient flood-basin accretion rates (Leeder, 1975; Wright and Marriott, 1996).

Variations in sedimentation, subsidence and erosion rates within a specific basin are controlled by both autochthonous and allochthonous processes. In alluvial basins, the sedimentation rate decreases across the floodplain with distance from the channel; this is an autochthonous process. The term 'pedofacies' refers to 'laterally contiguous bodies of sedimentary rocks that differ in their contained laterally contiguous palaeosols as a result of their distance (during formation) from areas of relatively high sediment accumulation' (Bown and Kraus, 1987). The pedofacies relationship explains why areas closest to the alluvial channels have thick, poorly developed palaeosol profiles, whereas more distal floodplain areas commonly exhibit different types and better developed soils.

Pedofacies relationships have been recognised in many ancient alluvial successions (Bown and Kraus, 1987; Smith, 1990; Alonso-Zarza et al., 1992b) and seem to be most applicable to overbank deposits (Kraus, 1997). However, they have not been seen in all floodplain palaeosol successions (Wright, 1992). Three main causes may explain the lack of pedofacies relationships in floodplain settings: (1) very low sedimentation rates may favour soils reaching a steady state, thus erasing pedofacies variations (Kraus, 1999); (2) floodplain aggradation may not only be the result of true suspension-load settling but also of deposition of laterally extensive crevasse-splay lobes (Behrensmeyer et al., 1995) and even by sheet floods containing pedogenic mud aggregates (Muller et al., 2004); and (3) in poorly drained soils, the intensity of soil development may mask the lateral variations in maturity (Kraus, 1997), and soil properties are more directly controlled by hydrology. In sum, pedofacies mostly result from changes in sedimentation rate at the same stratigraphical level, although they can also involve differences in depth to the water table at different locations on the floodplain.

Changes in floodplain aggradation through stratigraphic sections (with time) can also be estimated. Wright and Marriott (1996) developed a quantitative and sophisticated model to estimate the rates of floodplain aggradation using calcrete-bearing palaeosols. These authors considered that the residence time of the sediments in the zone of active pedogenesis is controlled by the frequency of the depositional events and by the thickness of sediment deposited during each event. Both can be represented in a plot to obtain different stages of pedogenic development. The plots do not allow absolute estimation of the sedimentation rates, but instead yield crude ranges of likely deposition rates, which can be used to interpret ancient floodplain successions. Rates of aggradation on floodplains of over 0.5 cm $year^{-1}$ seem to limit soil formation in alluvial valleys from the Great Plains (Daniels, 2003).

Calcrete reworking is very common on floodplains and forms lenses of reworked calcrete deposits (Allen and Williams, 1979). Very commonly, only poorly developed calcretes (Stage 1 or II) are reworked because disconnected nodules are more easily eroded, transported and redeposited in a nearby area of the river system in channels, or on levees, as in the Permian and Triassic of Minorca (Gómez-Gras and Alonso-Zarza, 2003). Reworking of the upper and softer horizons of soils must have been a common process in sediments older than Middle Palaeozoic due to the lack of a rooted vascular plant cover, which favours the mobility of the upper soil horizons (Marriott and Wright, 2006). Although not *in situ*, reworked calcrete deposits also provide evidence of differences in floodplain accretion and erosion rates.

The sedimentation rate may, however, also vary in relation with allochthonous causes such as the accommodation space available or the tectonic regime of the basin. The characteristics of calcrete-bearing palaeosols within a specific alluvial basin may also reflect changes in the accommodation space that are a response to up-dip changes in the subsidence rate, possible down-dip eustatic effects (McCarthy et al., 1999) and climate (Shanley and McCabe, 1994). The interplay of these three factors (tectonism, climate and eustasy) makes the establishment of unique models of sequence stratigraphy in terrestrial basins very difficult. Wright and Marriott (1993) proposed a simple architectural/pedogenic model for a fluvial sequence deposited during a third-order cycle of base-level fall and rise, in which the only autochthonous control is eustasy. During lowstands, well-developed and well-drained calcrete-bearing soils form on the terraces produced by channel incision. In the initial stages of the transgressive systems tract, the rate of creation of accommodation space is low, which favours the development of hydromorphic soils. A later rise in sea level accounts for the formation of soils that are weakly developed but which are well drained since the increased accommodation rate leads to high levels of storage of floodplain sediments. During the highstand phase, accommodation is reduced and floodplain accretion rates drop, favouring better developed soils. This model may be considered a first approach to the establishment of detailed sequence stratigraphy in terrestrial basins, but has to be improved by taking into account the position of the systems tracts in the basin, and testing it in areas where coeval marine and non-marine strata occur (Shanley and McCabe, 1994). Gómez-Gras and Alonso-Zarza (2003) have developed a model, similar to that proposed by Wright and Marriott (1993), that includes the type of reworked calcrete deposits along the Permian and Triassic fluvial deposits. The reworked deposits form preferably during the transgressive stages, where the high rates of aggradation of the floodplain favour weakly developed calcretes, which can be more easily reworked.

Where it is possible to isolate other allochthonous factors, tectonism can be revealed as the most likely control on calcrete-bearing palaeosol characteristics, due to its influence on the sedimentation rate and because it generates different geomorphological settings. In the study of the Capella Formation in the Spanish Pyrenees, Atkinson (1986) showed that variations in the subsidence rate along the basin caused important differences in the rate of floodplain aggradation, and therefore in the degree of development of the palaeosols. The morphology of the basin may also be reflected in the morphology of the palaeosols. In the southern Rio Grande rift, symmetrical basins contain Stage II and III palaeosols that are laterally continuous, and about five times more abundant than in asymmetrical basins, where palaeosols lack well-developed horizons and consist mostly of spaced rhizoliths (Mack and James, 1993). This reflects the different sedimentation rates between the two types of basins. In the Triassic rift of the Iberian Ranges in Spain (Alonso-Zarza et al., 1999), calcrete-bearing palaeosols developed on the footwall zones are scarce and well developed (Stage V), whereas the number of palaeosols is higher in the hanging wall, but these soils are less developed (up to Stage III). This is due to the higher subsidence rates in the hanging wall. Differences in the characteristics of palaeosols developed on the footwall and hanging wall are not limited to the degree of development. Mack et al. (2000) found that authigenic carbonates in general, and palaeosol carbonate in particular, that were formed in footwall-derived alluvial fans, show higher $\delta^{13}C$ values than those formed in hanging walls. This may reflect differences in either the ratio of C_3 to C_4 vegetation, or floral density.

Climate also has a great influence on the likelihood of calcrete formation and controls some of the features. The potential to use calcretes to estimate palaeorainfall has been suggested (e.g., Retallack, 1994), on the basis of a correlation between the depth to the top of the calcic horizon and the mean annual rainfall. Retallack (1994, 2000) used a data set compiled from Aridisols, Inceptisols and Mollisols. Royer (1999) questioned the existence of a strong correlation. However, a strong correlation was recorded by Stiles et al. (2001) for calcic Vertisols in Texas, although these Vertisols retain carbonate at higher levels of precipitation (Nordt et al., 2006). This is important because many calcretes in the stratigraphic record are associated with palaeo-Vertisol profiles. Khadkikar et al. (2000), based on Late Quaternary calcrete-bearing soils from Gujarat, India, identified different types of calcretes, including calcic Vertisols, related to distinctly different climates. These authors also identified the different micromorphological characteristics of the calcretes associated with these different climates.

Clearly, climate controls the degree of development of palaeosols, in part because of its influence on sedimentation rates, and also because the climatic effect may overprint the effects of other controls (Tanner, 2010). Stable-isotope analyses are now considered a crucial tool for obtaining palaeoclimatic information (Tanner, 2010). In palaeosols from the late Eocene of India, for example, the C and O isotopes reveal that calcrete formation occurred during drier intervals, whereas the host mudstones were deposited during warm and wet intervals (Singh and Lee, 2007).

Tanner and Lucas (2006) demonstrated that the upward stratigraphic change from kaolinitic palaeosols with gley features (in Carnian palaeosols) to Stage IV calcretes (in Norian palaeosols) in the Chinle Group in the southwestern USA relates to gradual aridification during the Upper Triassic. However, in many situations it is difficult to determine if the variation in the type and development of calcretes is due to intra- or extrabasinal forces. For example, the environmental changes reflected in the calcrete-bearing palaeosols in the Triassic of NW Argentina respond to the geomorphological position (catenary relationship) and the structural setting of the palaeosol (Tabor et al., 2006).

Calcrete-bearing soils and palaeosols are common in arid and semi-arid alluvial fans. Their formation takes place on stable fan surfaces, on which levels of erosion or sedimentation are reduced. This stability may occur over the whole fan due to a climatic change, or because the locus of deposition/erosion has moved by entrenchment, avulsion or dissection (Wright, 1992), which will create different distributions of the soils along the fan (Wright and Alonso-Zarza, 1990). Non-entrenched fans show weakly developed soils in proximal areas and more developed ones in the distal parts (according to McCraw, 1968). In entrenched fans, either partially or totally, the isolated (entrenched) areas will show more prolonged pedogenesis, while the areas where sedimentation takes place will show less-developed soils (McCraw, 1968; Talbot and Williams, 1979). In cases where climatic changes have caused the retardation or cessation of sedimentation, soils will develop on the whole fan surface (Talbot and Williams, 1979). Similar patterns can be observed if the causes of non-sedimentation are induced by base-level changes (Gile et al., 1981).

In many cases, alluvial basins are closed drainage systems in which the central areas are occupied by lakes, either fresh-water or saline. It seems that the existence of a long-lasting evaporite basin is a major control on the formation of thick groundwater calcretes (Jutras et al., 2007). Closed carbonate or evaporitic lacustrine basins commonly show low relief, flat topographies; small changes in the amount of surficial water input, or in climate, therefore favour movements of groundwaters that result in the mixing of pedogenic, groundwater and palustrine or playa water. Consequently, it can be difficult to differentiate amongst pedogenic and groundwater calcretes on one hand, and palustrine carbonates on the other (Alonso-Zarza, 2003). Figure 7 illustrates how a gradual rise of the water

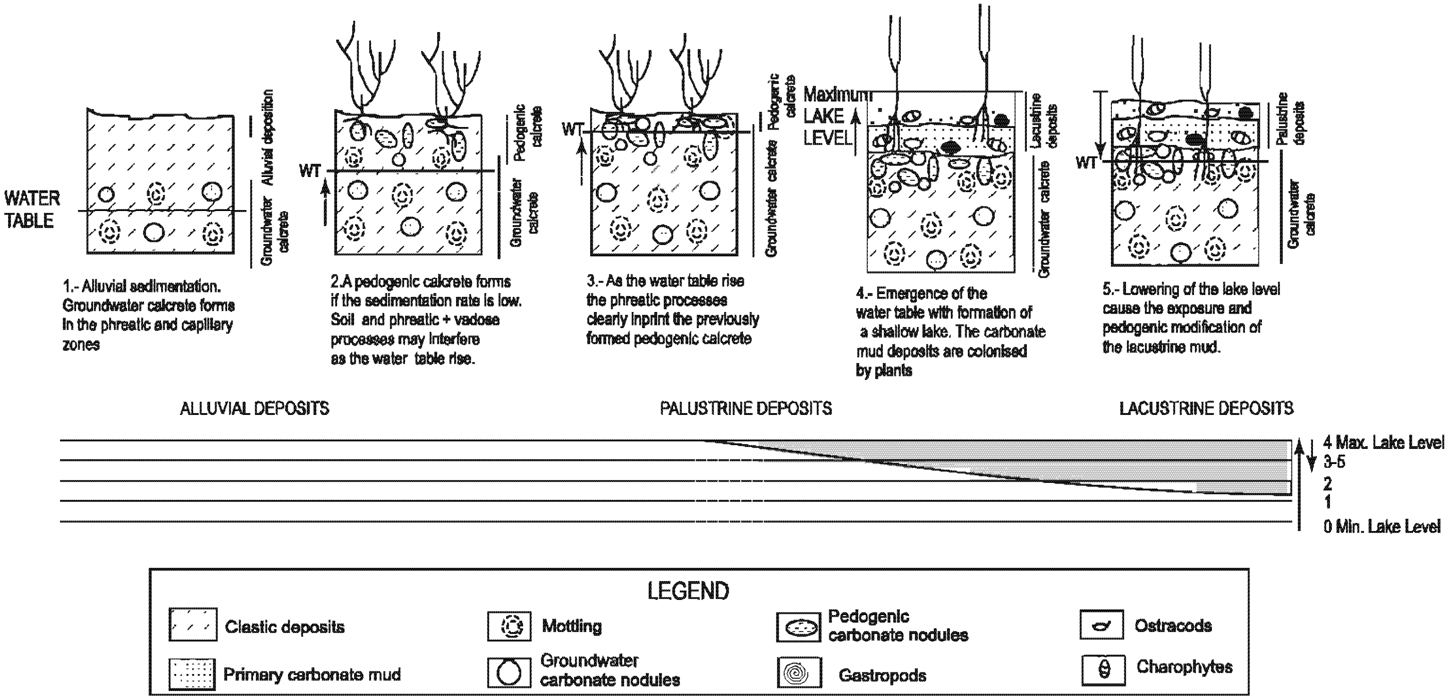

Figure 7 Sketch of the lateral and vertical transitions of alluvial, palustrine and lacustrine deposits in a distal alluvial and/or floodplain environment. The different situations 1–5 indicate the position of the water table (Modified from Alonso-Zarza, 2003).

table results first in the modification of previously formed pedogenic carbonates by groundwater, and later in the emergence of a free water body on the surface. A further lowering of the water table causes the previously deposited lacustrine sediments to be situated in either the vadose or the phreatic zone, where they can be modified by either pedogenic or groundwater process. The transition from pedogenic to groundwater calcretes, ending in palustrine carbonates, is seen in the Tertiary from the Duero Basin (Armenteros and Huerta, 2006) and has been interpreted as the result of a progressive decrease in sediment supply, very probably controlled by climate.

Calcretes, and indeed all other types of palaeosols, are also commonly associated with unconformities. Therefore, they can often be used as sequence boundaries (McCarthy and Plint, 1998) in non-marine deposits. The maturity of the palaeosols may give an idea of the type and range of the sedimentary discontinuity. In the Mississippian of the Appalachian Basin, Etthenson et al. (1988) described well-developed and thick caliche profiles on disconformities related to important tectonic activity or regional regressions; less mature profiles occur within sedimentary discontinuities related to local regressions. Laminar calcretes are frequently located at important unconformities, such as in Minorca, where Carboniferous deposits are penetrated and overlain by a laminar calcrete developed prior to the deposition of the Permian red-bed deposits (Gómez-Gras and Alonso-Zarza, 2003). In the Teruel Basin in NE Spain, a laminar calcrete, probably early Palaeogene in age, developed on Jurassic marine deposits. This calcrete contains *Microcodium* and probably marks the Mesozoic/Cenozoic boundary (Alonso-Zarza and Arenas, 2004). Calcretes as indicators of unconformities are also recognised and used in subsurface stratigraphy (Hanneman et al., 1994; Hanneman and Wideman, 2006, 2010), providing one more element of basin-architecture analysis in buried deposits.

10. Conclusions

Calcretes are near-surface accumulations of calcium carbonate of pedogenic origin or formed by laterally flowing, shallow groundwaters, mainly in alluvial aquifers. Earlier views that pedogenic calcretes were formed by precipitation from groundwaters have long since been dismissed. Now we better appreciate that they truly are pedogenic precipitates, with carbonate sourced largely from the atmosphere, and with precipitation triggered in many cases by the activities of roots and fungi. In some cases, the biochemical pathways leading to calcite formation are complex. Progressive models for pedogenic profile development originally envisaged a simple linear evolution, but Quaternary examples have revealed complex stratigraphies controlled by climate, amongst other factors, that induce intervals of erosion, deposition, vegetation changes and carbonate accumulation. As a result, a more dynamic model has developed that views calcrete profiles as sensitive to environmental changes (Figure 6). Under certain circumstances, calcrete can be removed from a profile, or moved to other levels within the profile as a consequence of changes in precipitation. As pedogenic calcretes are abundant in some ancient alluvial–fluvial successions, their occurrence and degree of development have been used to develop complex models of landscape evolution and to assess the relative importance of large-scale controls, such as tectonism and eustasy.

Geochemical studies, especially of the stable C and O isotopes, have suggested many important applications for pedogenic calcretes. Analysis of these isotopes can provide information on palaeotemperatures, palaeoatmospheric composition and palaeovegetation types. Due to the relative abundance of pedogenic calcretes in the stratigraphic record, we have glimpses of the history of these factors in deep time.

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